

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-029795

(43)Date of publication of application : 02.02.1999

(51)Int.Cl.

C11D 7/18  
B08B 3/04  
B08B 3/08  
C02F 1/50  
C02F 1/50  
C02F 1/50  
H01L 21/304

(21)Application number : 09-197781

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(22)Date of filing : 08.07.1997

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**(54) CLEANING WATER FOR ELECTRONIC MATERIAL, ITS PREPARATION, AND CLEANING OF ELECTRONIC MATERIAL****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To obtain a cleaning water for electronic materials which can clean electronic materials, such as semiconductor substrates, contaminated with a metal component, such as copper, in an efficient manner with high percentage removal of contaminants and, after cleaning, causes only a light waste water treatment burden.

**SOLUTION:** This cleaning water for electronic materials is an ozone-contg. ultrapure water that has a standard redox potential of 1,200 to 1,500 mV and a pH value of 3.5 to 6.5. The process for preparing the cleaning water for electronic materials comprises either bringing ultrapure water, which has been previously adjusted to pH3.5 to 6.5 by the addition of an acid, into contact with ozone gas through a gas permeable membrane to prepare a water contg. dissolved ozone, or bringing ozone gas into contact with ultrapure water through a gas permeable membrane to prepare a water contg. dissolved ozone, followed by addition of an acid to adjust the water to pH3.5 to 6.5. The method for cleaning electronic materials comprises bringing an electronic material contaminated with a metal component into contact with the cleaning water for electronic materials.

**LEGAL STATUS**

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] Wash water for electronic ingredients characterized by being the ultrapure water containing ozone, for standard oxidation reduction potential being 1,200–1,500mV, and pH being 3.5–6.5.

[Claim 2] The manufacture approach of the wash water for electronic ingredients according to claim 1 characterized by contacting the ultrapure water which added the acid beforehand and adjusted pH to 3.5–6.5, and ozone gas through a gas permeable membrane.

[Claim 3] The manufacture approach of the electronic ingredient wash water according to claim 1 characterized by adding an acid in the ozone dissolution water which ultrapure water and ozone gas were contacted through the gas permeable membrane, and prepared them, and adjusting pH to it 3.5–6.5.

[Claim 4] The washing approach of the electronic ingredient characterized by contacting the electronic ingredient polluted with a part for a metal to the wash water for electronic ingredients according to claim 1.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the wash water for electronic ingredients. This invention relates to the wash water for [ with the waste fluid processing burden light / that electronic ingredients, such as a semi-conductor substrate, can be especially washed with an efficient high contamination elimination factor / after washing / which was polluted by the amount of /, such as copper which is easy to adhere and is hard to dissolve, / metal ] electronic ingredients in more detail.

[0002]

[Description of the Prior Art] Conventionally, after washing on the front face of a semi-conductor in an LSI production process etc. is mainly immersed in the solution which mixed and prepared dark aqueous ammonia or concentrated hydrochloric acid, and hydrogen peroxide solution and ultrapure water in a semi-conductor, it has been immediately performed by the approach of calling the so-called RCA cleaning method (W. Kern and D.A. Puotinen, RCA Review, the 81st volume, 187-205 pages, June, 1970 issue) which is ultrapure water. In order to remove a part for the metal on the front face of a semi-conductor especially, the method of being ultrapure water and rinsing concentrated hydrochloric acid, hydrogen peroxide solution, and ultrapure water after mixing and being immersed in the warmed solution, with 1:1:6 thru/or about 1:1:4 ratio, by the volume, was used. If this approach is used, even if the amount of [, such as copper, ] metal has adhered to the semi-conductor substrate front face before washing, it is said, for example that it is removable even to the concentration said to hardly have a bad influence on the engine performance of LSI. Moreover, the method of acquiring the clean surface is proposed by JP,58-100433,A by washing with the solution which blew ozone into the solution of hydrochloric acid which replaced with hydrogen peroxide solution and mixed ultrapure water with concentrated hydrochloric acid about to 1:4 by capacity using ozone. However, by such approach, in order to use an acid, high-concentration alkali, and a high-concentration hydrogen peroxide so much, while these chemicals are discharged in waste fluid and a great burden is placed on neutralization, precipitate processing, etc. in waste water treatment, a lot of sludge is generated. That is, in order to secure the cleanliness of a semi-conductor substrate front face, great costs are needed for a chemical and waste fluid processing. For this reason, while decreasing the amount of a chemical required for washing on the front face of a semi-conductor, development of the washing approach which can mitigate the burden of waste fluid processing is tried. For example, the method of processing ultrapure water using the anode water or cathode water electrolyzed and obtained is proposed by JP,9-19668,A, irradiating a supersonic wave at a processed material. According to this approach, it is possible to reduce the amount of the chemical used which needs waste fluid processing, but if an acid is not added so that it may be set to about two pH, there is a problem that the elimination factor for a metal does not fully improve. This invention persons proposed the washing approach using the water solution of pH 1-3 containing the chlorine compound of an oxidizing quality in JP,8-316187,A previously. According to this approach, the semi-conductor substrate etc. could be washed, high surface cleanliness could be obtained, processing of waste fluid was also comparatively easy, but the

washing approach which can make waste fluid processing still easier came to be searched for using the wash water still nearer to neutrality, maintaining an equivalent cleaning effect.

[0003]

[Problem(s) to be Solved by the Invention] This invention is made for the purpose of being able to wash electronic ingredients, such as a semi-conductor substrate polluted by the amount of [ , such as copper, ] metal, with an efficient high contamination elimination factor, and offering the light wash water for electronic ingredients of the waste fluid processing burden after washing.

[0004]

[Means for Solving the Problem] The wash water which this invention persons made ultrapure water contain ozone as a result of repeating research wholeheartedly that the above-mentioned technical problem should be solved, and set standard oxidation reduction potential to 1,200mV or more The cleaning effect which was excellent even if pH was 3.5-6.5 comparatively near neutrality is demonstrated. Such wash water By making ozone gas contact through a gas permeable membrane, after adding an acid to ultrapure water Or by adding an acid in the ozone dissolution water which ultrapure water and ozone gas were contacted through the gas permeable membrane, and prepared them, it finds out that it can manufacture easily and came to complete this invention based on this knowledge. Namely, this invention is the ultrapure water containing (1) ozone, and standard oxidation reduction potential is 1,200-1,500mV. the wash water for electronic ingredients characterized by pH being 3.5-6.5, and (2) -- the ultrapure water and ozone gas which added the acid beforehand and adjusted pH to 3.5-6.5 The manufacture approach of the wash water for electronic ingredients given in \*\* (1) term characterized by making it contact through a gas permeable membrane, (3) in the ozone dissolution water which ultrapure water and ozone gas were contacted through the gas permeable membrane, and prepared them The manufacture approach of the electronic ingredient wash water given in \*\* (1) term characterized by adding an acid and adjusting pH to 3.5-6.5, And the washing approach of the electronic ingredient characterized by contacting the electronic ingredient polluted with a part for (4) metals to the wash water for electronic ingredients given in \*\* (1) term is offered.

[0005]

[Embodiment of the Invention] The wash water for electronic ingredients of this invention is ultrapure water containing ozone, standard oxidation reduction potential is 1,200-1,500mV, and pH is wash water of 3.5-6.5. As an electronic ingredient which can be washed with the wash water for electronic ingredients of this invention, the silicon substrate for semi-conductors, the glass substrate for liquid crystal, etc. can be mentioned, for example. It can obtain by there being especially no limit in the manufacture approach of the ultrapure water used for this invention, for example, processing primary pure water, such as deionized water and distilled water, using a reverse osmotic membrane, ultrafiltration membrane, a membrane filter, etc. The electrical resistivity in 25 degrees C is 18.0 or more M omega-cm, and, as for the ultrapure water used for this invention, it is desirable that organic carbon is 10micro less thang/l., and copper and iron are 0.02micro less thang/l., respectively. In this invention, although ozone gas and ultrapure water are contacted through a gas permeable membrane and ozone dissolution water is prepared, after preparing ozone dissolution water previously, using the ultrapure water which added the acid to ultrapure water beforehand and was adjusted to pH 3.5-6.5 at that time, an acid is added, it adjusts to pH 3.5-6.5, and the wash water for electronic ingredients of this invention is manufactured. Since ozone is stable at an acidity side, former one is a desirable approach among the above-mentioned approaches. In this invention, an acid is beforehand added to ultrapure water and pH is adjusted to 3.5-6.5. There is especially no limit in the acid to be used, for example, a hydrochloric acid, a nitric acid, a sulfuric acid, a hydrofluoric acid, etc. can be mentioned. In these, a hydrochloric acid can be used especially suitably. The amount of the hydrochloric acid used as pH of ultrapure water is less than 3.5 increases beyond the need, and the amount of the alkali used for neutralization of waste fluid in connection with it and the amount of the sludge generated by waste fluid processing increase. When pH of ultrapure water exceeds 6.5, it is not easy to raise standard oxidation reduction potential to 1,200mV or more, and since the copper contamination which is a candidate for removal approaches the field stabilized as a copper hydroxide, there is a possibility that the cleaning effect of the wash water

for electronic ingredients may fall.

[0006] Although there is especially no limit in the gas permeable membrane used in this invention, if ozone resistance is taken into consideration, poly membranes, such as polytetrafluoroethylene, are suitable. Ozone gas can be generated by there being especially no limit in the generating approach of ozone gas, for example, carrying out silent discharge or electrolyzing ultrapure water in dust removing, the dehumidified air, or oxygen gas. Ozone shifts into ultrapure water via a gas permeable membrane by passing ultrapure water to the liquid side of a gas permeable membrane, and passing ozone gas to a gas side. The wash water for electronic ingredients of this invention contains ozone, and standard oxidation reduction potential is 1,200–1,500mV. It is the value which converted into normal-hydrogen-electrode criteria the value which the electrode was used for standard oxidation reduction potential, and was measured at 25 degrees C here. There is a possibility that removing [ of the low copper of a part for the metal of an electronic ingredient front face and an ionization tendency etc. ]

standard oxidation reduction potential may become being less than 1,200mV inadequate. Even if standard oxidation reduction potential exceeds 1,500mV, the improvement in a cleaning effect which usually balances the rise of standard oxidation reduction potential is not found. [0007] There is especially no limit in the approach of making the electronic ingredient polluted with a part for a metal contacting, and it can choose suitably the wash water for electronic ingredients of this invention as it according to the adhesion condition for a metal etc. For example, it can be immersed in the wash water for electronic ingredients, and batch washing of the electronic ingredient polluted with a part for a metal can be carried out, or single-wafer-processing washing which washes one electronic ingredient at a time can be performed. The spin cleaning method which kicks the wash water for electronic ingredients in a sink is mentioned rotating the electronic ingredient polluted with a part for a metal as an example of single-wafer-processing washing. Furthermore, if needed, vibration by the supersonic wave can be given to the wash water for electronic ingredients, and a cleaning effect can be heightened. According to this invention, the amount of the chemical used for washing of an electronic ingredient can be decreased sharply, and a high cleaning effect can be acquired, and the waste fluid processing after washing of an electronic ingredient becomes easy further. That is, since the conventional washing waste fluid is discharged in the high-concentration condition which contained the hydrochloric acid and the hydrogen peroxide in large quantities, neutralization processing and decomposition processing are required, and the chemical of an amount comparable as having used it for preparation of a penetrant remover further also in waste fluid processing is needed. In this invention, the liquid of pH 3.5–6.5 containing ozone will be discharged, for example, if ozone is decomposed by activated carbon treatment etc., it will be water quality reusable enough as raw water for ultrapure water.

[0008]

[Example] Although an example is given to below and this invention is further explained to it at a detail, this invention is not limited at all by these examples.

Nine contamination wafers with which copper adhered to the front face were produced by drying a silicon wafer with example 1 diameter of 6 inches, after being immersed in the water containing 10microg [ /l. ] copper and 0.5% of the weight of fluoric acid for 3 minutes. In order to ask for the copper concentration before washing processing, three of sheets [ them ] were sampled and surface copper concentration was measured with the fluoric acid vapor-decomposition-atomic absorption method. Consequently, the averages of the copper concentration of three contamination wafers were  $1.93 \times 10^{12}$  atom /  $\text{cm}^2$ . The ultrapure water which added the hydrochloric acid and was set to pH4.0 was made to contact ozone gas through the gas permeable membrane made from Teflon, and the wash water for electronic ingredients whose standard oxidation reduction potential is 1,380mV was obtained. About three contamination wafers, the contamination wafer was rotated by 500rpm, the above-mentioned wash water for electronic ingredients was poured by part for 700ml/, and spin washing was performed for 3 minutes. Then, it dried, after rinsing with ultrapure water. The concentration of the copper on the front face of a wafer after desiccation was measured with the fluoric acid vapor-decomposition-atomic absorption method. The averages of three sheets were two or less  $1.0 \times 10^{10}$  atom /  $\text{cm}^2$ ,

and the elimination factor of the copper on the front face of a wafer was 99.5% or more. Instead of the wash water for electronic ingredients of example of comparison 1 this invention, the contamination wafer was washed on condition that 70A and 5V using the electrolysis anode water prepared by part for 3.5l./of the rates of flow. The above-mentioned electrolysis anode water which was made to rotate a contamination wafer by 500rpm, added the hydrochloric acid, and was adjusted to pH4.0 about three contamination wafers produced in the example 1 was poured by part for 700ml/, and spin washing was performed for 3 minutes. Then, it dried, after rinsing with ultrapure water. The concentration of the copper on the front face of a wafer after desiccation was measured with the fluoric acid vapor-decomposition-atomic absorption method. The averages of three sheets were  $2.14 \times 10^{11}$  atom /  $\text{cm}^2$ , and the elimination factor of the copper on the front face of a wafer was 88.9%.

[0009]

[Effect of the Invention] The wash water for electronic ingredients of this invention can have few amounts of the drugs to be used, can be manufactured easily, can wash the front face of the electronic ingredient polluted with a part for a metal at high washing effectiveness, can remove a part for a metal, and can process easily the waste fluid generated further.

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[Translation done.]

(19) 日本国特許庁 (J P)

## (12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-29795

(43) 公開日 平成11年(1999) 2月2日

(51) Int.Cl. <sup>6</sup>	識別記号	F I
C 1 1 D 7/18		C 1 1 D 7/18
B 0 8 B 3/04		B 0 8 B 3/04 Z
		3/08 Z
C 0 2 F 1/50	5 3 1	C 0 2 F 1/50 5 3 1 R
	5 4 0	5 4 0 A

審査請求 未請求 請求項の数4 F D (全 4 頁) 最終頁に続く

(21) 出願番号 特願平9-197781

(22) 出願日 平成9年(1997) 7月8日

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(54) 【発明の名称】 電子材料用洗浄水、その製造方法及び電子材料の洗浄方法

## (57) 【要約】

【課題】銅などの金属分により汚染された半導体基板などの電子材料を、効率よく高い汚染物除去率で洗浄することができ、かつ洗浄後の廃液処理負担の軽い電子材料用洗浄水を提供する。

【解決手段】オゾンを含む超純水であって、標準酸化還元電位が1,200～1,500mVであり、pHが3.5～6.5であることを特徴とする電子材料用洗浄水、あらかじめ酸を添加してpHを3.5～6.5に調整した超純水とオゾンガスを、ガス透過膜を介して接触させるか、又は、オゾンガスと超純水をガス透過膜を介して接触させて調製したオゾン溶解水に酸を添加してpHを3.5～6.5に調整することを特徴とする該電子材料用洗浄水の製造方法、及び、金属分で汚染された電子材料を、該電子材料用洗浄水と接触させることを特徴とする電子材料の洗浄方法。



## 【特許請求の範囲】

【請求項 1】 オゾンを含む超純水であって、標準酸化還元電位が 1,200~1,500mV であり、pH が 3.5~6.5 であることを特徴とする電子材料用洗浄水。

【請求項 2】 あらかじめ酸を添加して pH を 3.5~6.5 に調整した超純水とオゾンガスを、ガス透過膜を介して接触させることを特徴とする請求項 1 記載の電子材料用洗浄水の製造方法。

【請求項 3】 超純水とオゾンガスをガス透過膜を介して接触させて調製したオゾン溶解水に、酸を添加して pH を 3.5~6.5 に調整することを特徴とする請求項 1 記載の電子材料用洗浄水の製造方法。

【請求項 4】 金属分で汚染された電子材料を、請求項 1 記載の電子材料用洗浄水と接触させることを特徴とする電子材料の洗浄方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、電子材料用洗浄水に関する。さらに詳しくは、本発明は、付着しやすく溶解しにくい銅などの金属分により汚染された、特に半導体基板などの電子材料を、効率よく高い汚染物除去率で洗浄することができ、かつ洗浄後の廃液処理負担の軽い電子材料用洗浄水に関する。

## 【0002】

【従来の技術】 従来、LSI 製造工程における半導体表面などの洗浄は、主として、濃アンモニア水又は濃塩酸と、過酸化水素水と超純水とを混合して調製した溶液に半導体を浸漬した後に超純水ですすぐ、いわゆる RCA 洗浄法 (W. Kern and D. A. Puotinen, RCA Review, 第 81 巻, 187~205 頁, 1970 年 6 月発行) と呼ばれる方法によって行われてきた。特に、半導体表面の金属分を除去するためには、濃塩酸、過酸化水素水、超純水を体積で 1:1:6 ないし 1:1:4 程度の比率で混合し、加温した溶液に浸漬後、超純水ですすぐ方法が用いられていた。この方法を使用すると、例えば、洗浄前に半導体基板表面に銅などの金属分が付着していても、LSI の性能にほとんど悪影響を与えないといわれる濃度にまで除去することができると言われている。また、特開昭 58-100433 号公報には、過酸化水素水に代えてオゾンを用い、濃塩酸と超純水を容量で 1:4 程度に混合した塩酸溶液に、オゾン吹き込んだ溶液で洗浄することにより清浄な表面を得る方法が提案されている。しかし、このような方法では、高濃度の酸、アルカリや過酸化水素を多量に使用するために、廃液中にこれらの薬品が排出され、廃液処理において中和や沈殿処理などに多大な負担がかかるとともに、多量の汚泥が発生する。すなわち、半導体基板表面の清浄度を確保するために、薬品及び廃液処理に多大な費用を必要とする。このために、半導体表面

の洗浄に必要な薬品の量を減少するとともに、廃液処理の負担を軽減し得る洗浄方法の開発が試みられている。例えば、特開平 9-19668 号公報には、被処理物に超音波を照射しながら超純水を電解して得たアノード水又はカソード水を用いて処理する方法が提案されている。この方法によれば、廃液処理に必要な薬品の使用量を低減することは可能であるが、pH 2 程度になるように酸を添加しなければ金属分の除去率が十分に向上しないという問題がある。本発明者らは、先に特開平 8-316187 号公報において、酸化性の塩素化合物を含む pH 1~3 の水溶液を用いる洗浄方法を提案した。この方法によれば、半導体基板などを洗浄して高い表面清浄度を得ることができ、廃液の処理も比較的容易であるが、同等の洗浄効果を維持しながら、さらに中性に近い洗浄水を用い、廃液処理を一層容易にすることができる洗浄方法が求められるようになった。

## 【0003】

【発明が解決しようとする課題】 本発明は、銅などの金属分により汚染された半導体基板などの電子材料を、効率よく高い汚染物除去率で洗浄することができ、かつ洗浄後の廃液処理負担の軽い電子材料用洗浄水を提供することを目的としてなされたものである。

## 【0004】

【課題を解決するための手段】 本発明者らは、上記の課題を解決すべく鋭意研究を重ねた結果、超純水にオゾンを含むせしめて標準酸化還元電位を 1,200mV 以上とした洗浄水は、pH が比較的中性に近い 3.5~6.5 であっても優れた洗浄効果を発揮し、このような洗浄水は、超純水に酸を添加したのちガス透過膜を介してオゾンガスを接触させることにより、又は、超純水とオゾンガスをガス透過膜を介して接触させて調製したオゾン溶解水に酸を添加することにより、容易に製造し得ることを見だし、この知見に基づいて本発明を完成するに至った。すなわち、本発明は、(1) オゾンを含む超純水であって、標準酸化還元電位が 1,200~1,500mV であり、pH が 3.5~6.5 であることを特徴とする電子材料用洗浄水、

(2) あらかじめ酸を添加して pH を 3.5~6.5 に調整した超純水とオゾンガスを、ガス透過膜を介して接触させることを特徴とする第(1)項記載の電子材料用洗浄水の製造方法、(3) 超純水とオゾンガスをガス透過膜を介して接触させて調製したオゾン溶解水に、酸を添加して pH を 3.5~6.5 に調整することを特徴とする第(1)項記載の電子材料用洗浄水の製造方法、及び、(4) 金属分で汚染された電子材料を、第(1)項記載の電子材料用洗浄水と接触させることを特徴とする電子材料の洗浄方法、を提供するものである。

## 【0005】

【発明の実施の形態】 本発明の電子材料用洗浄水は、オゾンを含む超純水であって、標準酸化還元電位が

1,200~1,500 mV、pHが3.5~6.5の洗浄水である。本発明の電子材料用洗浄水により洗浄することができる電子材料としては、例えば、半導体用シリコン基板、液晶用ガラス基板などを挙げることができる。本発明に用いる超純水の製造方法には特に制限はなく、例えば、脱イオン水、蒸留水などの1次純水を、逆浸透膜、限外ろ過膜、精密ろ過膜などを用いて処理することによって得ることができる。本発明に用いる超純水は、25℃における電気抵抗率が18.0 MΩ・cm以上であり、有機体炭素が10 μg/リットル以下であり、銅及び鉄がそれぞれ0.02 μg/リットル以下であることが好ましい。本発明においては、オゾンガスと超純水をガス透過膜を介して接触させてオゾン溶解水を調製するが、その際、予め超純水に酸を添加してpH 3.5~6.5に調整した超純水を用いるか、又は、先にオゾン溶解水を調製したのち、酸を加えてpH 3.5~6.5に調整して、本発明の電子材料用洗浄水を製造する。オゾンは酸性側で安定であるので、上記方法のうち前者の方が好ましい方法である。本発明においては、超純水にあらかじめ酸を添加してpHを3.5~6.5に調整する。使用する酸には特に制限はなく、例えば、塩酸、硝酸、硫酸、フッ化水素酸などを挙げることができる。これらの中で、塩酸を特に好適に使用することができる。超純水のpHが3.5未満であると、使用する塩酸の量が必要以上に多くなり、それに伴って廃液の中和に用いるアルカリの量や、廃液処理により発生する汚泥の量が多くなる。超純水のpHが6.5を超えると、標準酸化還元電位を1,200 mV以上に上げることが容易でなく、また、除去対象である銅汚染物が銅水酸化物として安定化する領域に近づくので、電子材料用洗浄水の洗浄効果が低下するおそれがある。

【0006】本発明において使用するガス透過膜には特に制限はないが、耐オゾン性を考慮すると、ポリテトラフルオロエチレンなどの高分子膜が好適である。オゾンガスの発生方法には特に制限はなく、例えば、除塵、除湿した空気又は酸素ガス中で無声放電したり、超純水を電気分解することにより、オゾンガスを発生させることができる。ガス透過膜の液体側に超純水を通過させ、気体側にオゾンガスを通過させることにより、オゾンはガス透過膜を経由して超純水中に移行する。本発明の電子材料用洗浄水は、オゾン含有し、標準酸化還元電位が1,200~1,500 mVである。ここに、標準酸化還元電位は、電極を用いて25℃で測定した値を標準水素電極基準に換算した値である。標準酸化還元電位が1,200 mV未満であると、電子材料表面の金属分、特にイオン化傾向の低い銅などの除去が不十分となるおそれがある。標準酸化還元電位が1,500 mVを超えても、通常は標準酸化還元電位の上昇に見合う洗浄効果の向上はみられない。

【0007】本発明の電子材料用洗浄水を、金属分で汚

染された電子材料と接触させる方法には特に制限はなく、金属分の付着状態などに応じて適宜選択することができる。例えば、金属分で汚染された電子材料を電子材料用洗浄水に浸漬してバッチ洗浄したり、電子材料を1枚ずつ洗浄する枚葉式洗浄を行うことができる。枚葉式洗浄の例としては、金属分で汚染された電子材料を回転させつつ電子材料用洗浄水を流しかけるスピン洗浄法が挙げられる。さらに、必要に応じて、電子材料用洗浄水に超音波による振動を与えて、洗浄効果を高めることができる。本発明によれば、電子材料の洗浄に使用する薬品の量を大幅に減少し、かつ高い洗浄効果を得ることができる。さらに、電子材料の洗浄後の廃液処理が容易になる。すなわち、従来の洗浄廃液は、塩酸や過酸化水素を大量に含んだ高濃度の状態で排出されるため、中和処理や分解処理が必要であり、廃液処理においてもさらに洗浄液の調製に使用したのと同程度の量の薬品が必要となる。本発明においては、排出されるのはオゾンを含んだpH 3.5~6.5の液であり、例えば、活性炭処理などでオゾンを分解してやれば、超純水用の原水として十分再利用できる水質である。

#### 【0008】

【実施例】以下に、実施例を挙げて本発明をさらに詳細に説明するが、本発明はこれらの実施例によりなんら限定されるものではない。

#### 実施例 1

直径6インチのシリコンウエハを、銅10 μg/リットルと0.5重量%のフッ酸を含む水に3分間浸漬したのち乾燥することによって、表面に銅が付着した汚染ウエハを9枚作製した。洗浄処理前の銅濃度を求めるため、その内の3枚を抜き取り、フッ酸蒸気分解-原子吸光法により表面の銅濃度を測定した。その結果、3枚の汚染ウエハの銅濃度の平均値は $1.93 \times 10^{12}$  原子/cm<sup>2</sup>であった。塩酸を添加してpH 4.0とした超純水を、テフロン製ガス透過膜を介してオゾンガスと接触せしめ、標準酸化還元電位が1,380 mVである電子材料用洗浄水を得た。3枚の汚染ウエハについて、汚染ウエハを500 rpmで回転させ、上記の電子材料用洗浄水を700 ml/分で流しかけ、3分間スピン洗浄を行った。その後、超純水ですすぎを行ったのち、乾燥した。乾燥後のウエハ表面の銅の濃度を、フッ酸蒸気分解-原子吸光法により測定した。3枚の平均値は $1.0 \times 10^{10}$  原子/cm<sup>2</sup>以下であり、ウエハ表面の銅の除去率は99.5%以上であった。

#### 比較例 1

本発明の電子材料用洗浄水の代わりに、70 A、5 Vの条件で、流速3.5リットル/分で調製した電解アノード水を用いて、汚染ウエハの洗浄を行った。実施例1で作製した3枚の汚染ウエハについて、汚染ウエハを500 rpmで回転させ、塩酸を添加してpH 4.0に調整した上記の電解アノード水を700 ml/分で流しかけ、3分間

スピン洗浄を行った。その後、超純水ですすぎを行ったのち、乾燥した。乾燥後のウエハ表面の銅の濃度を、フッ酸蒸気分解—原子吸光法により測定した。3枚の平均値は  $2.14 \times 10^{11}$  原子/cm<sup>2</sup> であり、ウエハ表面の銅の除去率は 88.9% であった。

【0009】

【発明の効果】本発明の電子材料用洗浄水は、使用する薬剤の量が少なく、容易に製造することができ、金属分で汚染された電子材料の表面を高い洗浄効率で洗浄して金属分を除去することができ、さらに発生する廃液を容易に処理することができる。

フロントページの続き

(51) Int. Cl.<sup>6</sup>

識別記号

C 0 2 F 1/50

5 5 0

H 0 1 L 21/304

3 4 1

F I

C 0 2 F 1/50

5 5 0 C

H 0 1 L 21/304

3 4 1 L